

## THE EFFECT OF POLYSILAZANE ON THE DENSIFICATION AND MECHANICAL PROPERTIES OF SiC<sub>f</sub>/SiC COMPOSITES

Alfian Noviyanto<sup>1,2</sup>

<sup>1</sup>Nano Center Indonesia, Jl. PUSPIPTEK, South Tangerang, Banten 15314 Indonesia

<sup>2</sup>Department of Mechanical Engineering, Mercuru Buana University,  
Jl. Meruya Selatan, Kembangan, Jakarta 11650, Indonesia

Email: a.noviyanto@nano.or.id

**Abstract** -- The effect of polysilazane on the densification and mechanical properties of SiC<sub>f</sub>/SiC composites was examined thoroughly. The polysilazane was infiltrated into the fiber area, followed by pyrolysis at 1450°C for 4 h in an argon atmosphere. Furthermore, the SiC fabrics contain the pyrolyzed polysilazane was infiltrated by β-SiC slurry and sintered at 1750°C for 2 h in an argon atmosphere. The density of SiC<sub>f</sub>/SiC composites with and without the addition of polysilazane was 2.65 and 3.05 g/cm<sup>3</sup>, respectively. The pores in the fiber area were observed for the SiC<sub>f</sub>/SiC composites with the addition of polysilazane. However, the fine-grained size in the matrix area was obtained by the addition of polysilazane. The average grain size of the SiC<sub>f</sub>/SiC composite with and without the addition of polysilazane was 253 and 740 nm, respectively. Indeed, the hardness of the matrix area for SiC<sub>f</sub>/SiC composites with the addition of polysilazane (31.6 ± 1.8 GPa) was higher compared to SiC<sub>f</sub>/SiC composites without polysilazane (27.4 ± 1.6 GPa).

**Keywords:** SiC<sub>f</sub>/SiC composites; Polysilazane; Density; Fine-grained; Hardness.

Copyright © 2020 Universitas Mercuru Buana. All right reserved.

Received: May 14, 2019

Revised: August 12, 2019

Accepted: August 22, 2019

### INTRODUCTION

The application of SiC fiber-reinforced SiC-matrix ceramic composites (SiC<sub>f</sub>/SiC) mainly in high-temperature, such as gas turbine, space shuttle, and a heat exchanger [1]. The condition happens because SiC<sub>f</sub>/SiC composites have exceptional properties in the chemical, thermal resistance and mechanical. Recently, low induced radioactivity and resistance under neutron irradiation of SiC<sub>f</sub>/SiC composites make its candidate for structural material in the fusion and advanced fission reactors [2, 3, 4]. However, the fabrication of dense SiC<sub>f</sub>/SiC composites is still challenging.

Chemical vapor infiltration (CVI) is the ideal fabrication method for SiC<sub>f</sub>/SiC composites due to the high purity of SiC<sub>f</sub>/SiC composites obtained by this method [5], [6]. However, it takes for a long time to fabricate the composites with porosity about 10-20%. The second method to fabricate SiC<sub>f</sub>/SiC composites is polymer impregnated pyrolysis (PIP) [7], [8]. This method uses polymer precursor instead of gas in the CVI. However, it requires multiple impregnations to obtain desirable density. The other method to fabricate SiC<sub>f</sub>/SiC composites is slurry infiltration combined with sintering [9], [10].

The mechanical properties of SiC<sub>f</sub>/SiC composites are also imperative for practical

application. Recently, polysilazane succeed in suppressing the grain growth of alumina and hafnia [11], [12]. The grain growth of SiC can be suppressed by the addition of polysilazane [13]. For instance, the grain size of monolithic SiC without the addition of polysilazane was 605 nm, which is higher compared to 161 nm with the addition of polysilazane. Moreover, SiC without the addition of sintering aids was successfully fabricated from pyrolyzed polysilazane as starting materials [14].

Therefore, with this background, we examine the effect of polysilazane on the densification and mechanical properties of SiC<sub>f</sub>/SiC composites. In this study, we combined the PIP and slurry infiltration method. The main goal of PIP is to infiltrate the polysilazane in the fiber area, whereas the β-SiC slurry to infiltrate the matrix area. The data on density, microstructure, and mechanical properties are examined to elucidate the effect of polysilazane on the SiC<sub>f</sub>/SiC composites.

### MATERIAL AND METHOD

Tyranno SA3 fabrics (Ube Industries LTD., Japan) was used as reinforcement. The fabrics have a woven structure and coated with pyrolytic carbon, with the thickness was 200 nm. Five layers of fabrics were infiltrated by liquid

polysilazane (KiON Ceraset Polysilazane 20, USA) in vacuum condition using special apparatus. This process was repeated five times. Furthermore, the fabrics containing polysilazane was pyrolyzed at 1450°C for 4 h in Ar atmosphere. The purpose of this infiltration to fill the inter fiber area with polysilazane that converted to Si, C and N after the pyrolysis process. Then, the pyrolyzed fabrics were infiltrated by slurry that contains  $\beta$ -SiC powder (>97.5% purity, 4620KE, NanoAmor Inc.), 12 wt.% sintering additives ( $Al_2O_3$  and  $Y_2O_3$ , with mass ration 60:40) and ethanol as a solvent. This mixture of  $\beta$ -SiC and sintering additives act as a matrix phase in the SiC<sub>f</sub>/SiC composite. Binder burns out was carried out in muffle furnace at 350°C for 2 h. Therefore, the ten layers of fabric were stacked in the graphite die and put in a hot pressing furnace. The sintering was performed at 1750°C for 2 h in Ar atmosphere under an applied pressure of 20 MPa. The SiC<sub>f</sub>/SiC composite without polysilazane was also prepared for comparison purposes. The sample with polysilazane and without polysilazane was named pSiC and nSiC, respectively.

The density of SiC<sub>f</sub>/SiC composites was measured with the Archimedes principle using distilled water as a medium. The microstructure of the SiC<sub>f</sub>/SiC composites was analyzed by scanning electron microscopy (SEM, S-4800, Hitachi, Japan). The grain size of the SiC<sub>f</sub>/SiC composite was estimated using the SEM image and analyzed statistically. A three-point bending test was performed using the ultimate testing machine (UTM AG-50E, Shimadzu, Japan). The composites were cut into 4x2x20 mm for bending test purposes. The bending strength of SiC<sub>f</sub>/SiC composites can be calculated using Equation (1).

$$\sigma = \frac{3}{2} \times \frac{P \cdot L}{b \cdot h^2} \quad (1)$$

where  $\sigma$  = bending strength (MPa), L = span distance (20 mm), b = breath of sample (mm) and h = height of sample (mm). Vickers indentation method was used to determine the hardness of SiC<sub>f</sub>/SiC composites using a hardness tester (MVK-H1, Mitutoyo, Japan). Ten indentations were made in the matrix area of the SiC<sub>f</sub>/SiC composite and for each hardness testing, the load and holding time was 1 kg and 10 s, respectively. The Hardness was calculated using Equation (2).

$$H = 0.0018544 \times \frac{P}{d^2} \quad (2)$$

where H = hardness (GPa), P = load (N) and d = average length of the two diagonals of indentation (mm). Prior to bending and hardness testing, the SiC<sub>f</sub>/SiC composites were polished using 1  $\mu$ m

diamond paste to remove the scratch from the samples.

## RESULTS AND DISCUSSION

Table 1 shows the theoretical, sintered and relative density of SiC<sub>f</sub>/SiC composites. nSiC showed the highest density, i.e., 3.05 g/cm<sup>3</sup> corresponding to 97.13% of relative density, while the density of pSiC was 2.65 g/cm<sup>3</sup>. In order to have a full understanding of the dissimilarity of density, microstructure examination was performed thoroughly.

Table 1. Theoretical, sintered and relative densities of SiC<sub>f</sub>/SiC composites

Sample	Theoretical density (g/cm <sup>3</sup> )	Sintered density (g/cm <sup>3</sup> )	Relative density (%)
pSiC	3.14	2.65 ± 0.07	84.39
nSiC	3.14	3.05 ± 0.01	97.13

Figure 1 shows the SEM images of SiC<sub>f</sub>/SiC composites after sintering at 1750°C for 2 h in Ar atmosphere under an applied pressure of 20 MPa. The typical sintering temperature for the liquid-phase sintering of SiC is 1800-2000°C [15, 16, 17]. However, since the high temperature is not desirable for industrial application, we choose a relatively low temperature at 1750°C in this study. Moreover, the other factor that influences the sintering temperature is sintering additives. On the other hand, the applied pressure during the sintering of SiC is necessary as a driving force for the densification and prevent grain growth. For instance, a paper reported that dense and nano-size of SiC was obtained with the applied pressure of 4.5 GPa [18]. However, the use of high pressure in SiC<sub>f</sub>/SiC composite is hindered due to the possible damage of the fiber, which affects the mechanical properties. The presence of fiber area and matrix area was observed in the SiC<sub>f</sub>/SiC composites both in the SiC<sub>f</sub>/SiC composites both in pSiC and nSiC.

The pores were observed clearly in the fiber area for pSiC, as shown in Figure 1 (b). Contrary, a relatively dense fiber area was obtained in the nSiC are shown in Figure 1 (a). These results agree with density calculation, as shown in Table 1. Since the viscosity is the main factor for the vacuum infiltration method [19], it more likely the viscosity of liquid polysilazane is too high to infiltrate the fiber area. In contrast, the  $\beta$ -SiC slurry succeeds to infiltrate the fiber area, which indicated by high density and dense structure as shown in Figure 1 (a). Meanwhile, we found the matrix area showed dense structure for both composites, reveals the  $\beta$ -SiC slurry cover the fabric adequately after vacuum infiltration process.

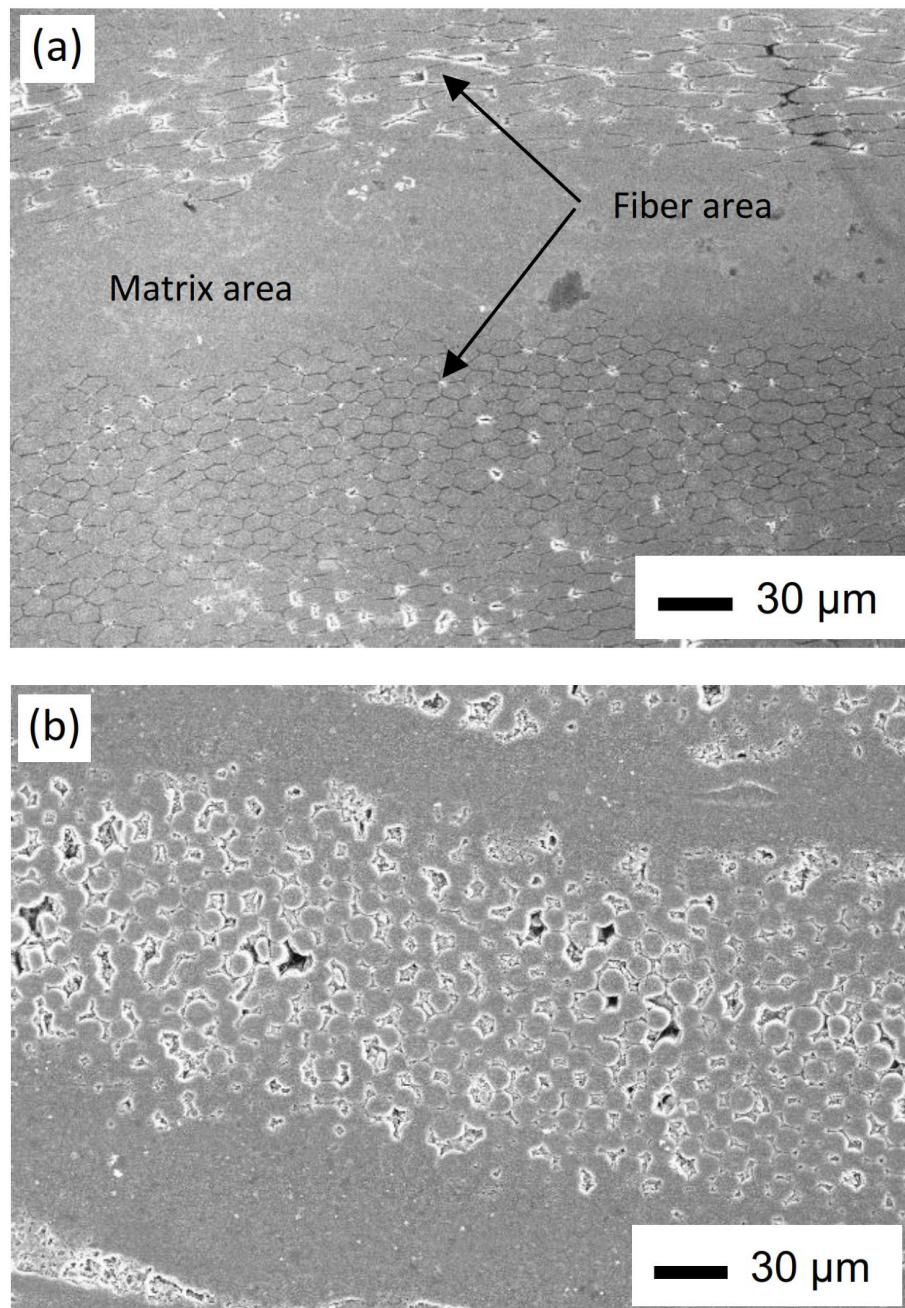


Figure 1. SEM Images of SiC<sub>f</sub>/SiC composites: (a) nSiC and (b) pSiC

Figure 2 shows the SEM images of the fiber area. The existence of fiber, pyrolytic carbon, closed pore, and liquid phase are shown in Figure 2 (a) for the nSiC sample. The liquid phase formed due to the reaction of sintering additive, i.e., Al<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub>, at high-temperature sintering. Nature covalent bonding of SiC makes it challenging to sinter without the addition of sintering additives through solid-state or liquid phase sintering mechanism. Therefore, the densification of the fiber area in nSiC can be understood by the presence of the liquid phase, as shown in Figure

2 (a). The shape of fiber change after sintering in nSiC samples. This is more likely due effect of the densification process and also external pressure that applied during sintering.

On the other hand, the absence of a liquid phase was observed in the pSiC (Figure 2 (b)). Indeed, the polysilazane that infiltrated to SiC fabrics did not contain any of sintering additives. Therefore, the sintering did not proceed to the last stage, resulting in the low density of pSiC, as shown in Table 1. However, the fiber shape in pSiC maintains the original shape.



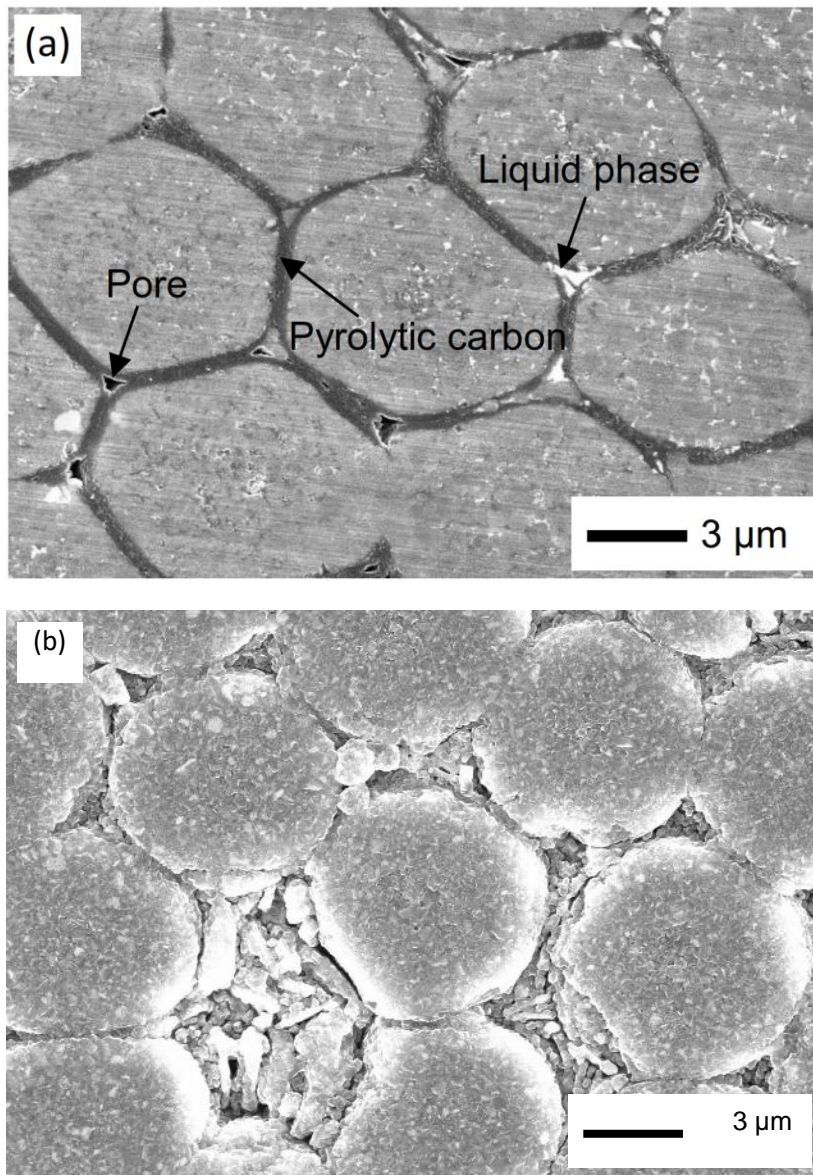


Figure 2. SEM Images of fiber area in the SiC<sub>i</sub>/SiC composites (a) nSiC and (b) pSiC

Table 2. Flexural strength and hardness of the SiC<sub>i</sub>/SiC composites

Sample	Flexural strength (MPa)	Hardness (GPa)
pSiC	143 ± 18	31.6 ± 1.8
nSiC	291 ± 42	27.4 ± 1.6

Figure 3 displays the grain size of SiC<sub>i</sub>/SiC composites in the matrix area. Indeed, the grain size of pSiC (Figure 3 (b)) is finer compared to nSiC (Figure 3 (a)). The average grain size for pSiC and nSiC was 253 and 740 nm, respectively. Although the source of the matrix area of those samples is similar, i.e., β-SiC and sintering additives, the resulting grain size was quite different. Therefore,

the grain size of pSiC is more likely influenced by the polysilazane. This result is in agreement with other reports that used polysilazane as additives [11, 12, 13].

The evidence of fine grain size is confirmed by hardness testing, as shown in Table 2. It showed that pSiC had higher hardness, i.e., 31.6 GPa, while the hardness of nSiC was 27.4 GPa. According to the Hall-Petch relationship, the small grain size resulting in higher hardness. However, the three-point bending test revealed the flexural strength of nSiC and pSiC was 291 and 143 MPa. Indeed, nSiC sample had higher flexural strength due to the density of SiC<sub>i</sub>/SiC composite is the one factor that affects flexural strength.

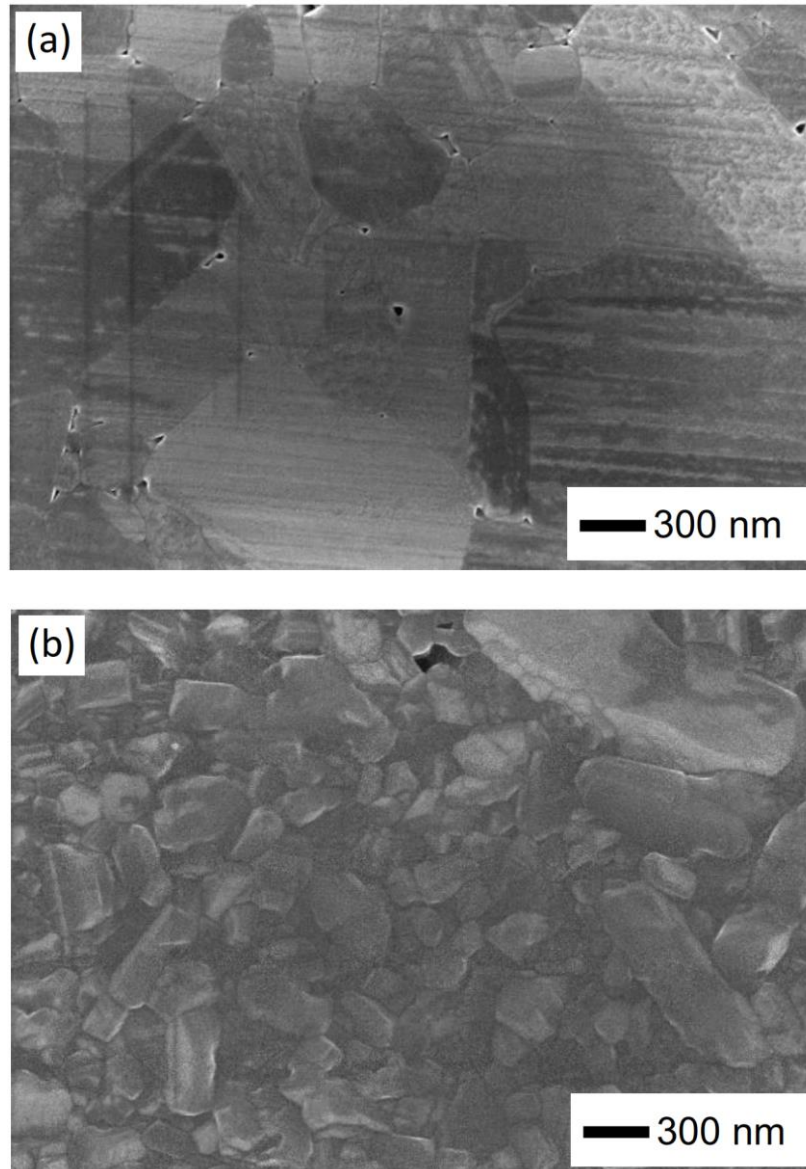


Figure 3. SEM Images of grain size in the matrix area of the SiC<sub>i</sub>/SiC composites (a) nSiC and (b) pSiC

### CONCLUSION

SiC<sub>i</sub>/SiC composites prepared by the infiltration of polysilazane and its effect on the densification and mechanical properties were examined thoroughly. It seems the polysilazane was not able to infiltrate deep into the fiber area, resulting in the existence of pores and low density in the fiber area of pSiC. However, the original shape of the fiber is maintained with the infiltration of polysilazane. The density of pSiC and nSiC was 2.65 and 3.05 g/cm<sup>3</sup>, respectively. In terms of mechanical properties, the hardness of the pSiC higher than nSiC, due to the finer grain size of pSiC. The grain size of pSiC was 253 nm, which increased five times from the original particle size.

However, the flexural strength of pSiC is lower compared to nSiC. Further study is needed to increase the density of SiC<sub>i</sub>/SiC composites with the addition of polysilazane.

### ACKNOWLEDGMENT

This research was supported by a grant from National Intensive Research System Innovation 2019 (INSINAS, No. 30/INS-1/PPK/E4/2019), the Ministry of Research, Technology and Higher Education, Republic of Indonesia.

### REFERENCES

- [1] J. S. Nadeau, "Very high pressure hot

- pressing of silicon carbide," *Am. Ceram. Bull.*, vol. 52, pp. 170–174, 1973.
- [2] A. Ortona *et al.*, "SiC-SiCf CMC manufacturing by hybrid CVI-PIP techniques: Process optimization," *Fusion Eng. Des.*, vol. 51–52, pp. 159–163, 2000. DOI: 10.1016/S0920-3796(00)00310-0
- [3] B. Riccardi *et al.*, "Issues and advances in SiCf/SiC composites development for fusion reactors," *J. Nucl. Mater.*, vol. 329–333, no. 1–3 PART A, pp. 56–65, 2004. DOI: 10.1016/j.jnucmat.2004.04.002
- [4] B. Riccardi, P. Fenici, A. Frias Rebelo, L. Giancarli, G. Le Marois, and E. Philippe, "Status of the European R&D activities on SiCf/SiC composites for fusion reactors," *Fusion Eng. Des.*, vol. 51–52, pp. 11–22, 2000. DOI: 10.1016/S0920-3796(00)00311-2
- [5] H. Araki, T. Noda, W. Yang, and A. Kohyama, "Homogeneity and flexural properties of SiC/SiC composites prepared by CVI method," *J. Nucl. Mater.*, vol. 307–311, no. 2 SUPPL., pp. 1210–1214, 2002. DOI: 10.1016/S0022-3115(02)01061-9
- [6] Y. Katoh, T. Nozawa, and L. L. Snead, "Mechanical properties of thin pyrolytic carbon interphase SiC-matrix composites reinforced with near-stoichiometric SiC fibers," *J. Am. Ceram. Soc.*, vol. 88, no. 11, pp. 3088–3095, 2005. DOI: 10.1111/j.1551-2916.2005.00546.x
- [7] X. Yang, L. Wei, W. Song, and C. Zhao-hui, "Effects of the single layer CVD SiC interphases on the mechanical properties of the C/SiC composites fabricated by PIP process," *Mater. Sci. Eng. A*, vol. 558, no. 7, pp. 451–455, 2012. DOI: 10.1016/j.msea.2012.08.026
- [8] A. Kohyama *et al.*, "High-performance SiC/SiC composites by improved PIP processing with new precursor polymers," *J. Nucl. Mater.*, vol. 283–287, no. PART I, pp. 565–569, 2000. DOI: 10.1016/S0022-3115(00)00270-1
- [9] P. Yonathan, J.-H. Lee, H.-T. Kim, and D.-H. Yoon, "Properties of SiC<sub>f</sub>/SiC composites fabricated by slurry infiltration and hot pressing," *Mater. Sci. Technol.*, vol. 27, no. 1, pp. 257–263, 2011. DOI: 10.1179/174328409X453172
- [10] T. Yano, K. Budiyo, K. Yoshida, and T. Iseki, "Fabrication of silicon carbide fiber-reinforced silicon carbide composite by hot-pressing," *Fusion Eng. Des.*, vol. 41, no. 1–4, pp. 157–163, 1998. DOI: 10.1016/S0920-3796(98)00094-5
- [11] E. Castellan, S. R. Shah, and R. Raj, "Compression creep of alumina containing interfacial silicon, carbon, and nitrogen, derived from a polysilazane precursor," *J. Am. Ceram. Soc.*, vol. 93, no. 4, pp. 954–958, 2010. DOI: 10.1111/j.1551-2916.2009.03515.x
- [12] S. Brahmmandam and R. Raj, "Novel composites constituted from hafnia and a polymer-derived ceramic as an interface: Phase for severe ultrahigh temperature applications," *J. Am. Ceram. Soc.*, vol. 90, no. 10, pp. 3171–3176, 2007. DOI: 10.1111/j.1551-2916.2007.01879.x
- [13] A. Noviyanto, D.-H. Yoon, Y.-H. Han, and T. Nishimura, "Effect of sintering atmosphere on the grain growth and hardness of SiC/polysilazane ceramic composites," *Adv. Appl. Ceram.*, vol. 115, no. 5, pp. 272–275, 2016. DOI: 10.1080/17436753.2015.1136124
- [14] A. Noviyanto and T. Nishimura, "Effect of Milling on the Densification of SiC-Based Composites from Polysilazane," *Makara J. Technol.*, vol. 20, no. 3, pp. 109–113, 2016. DOI: 10.7454/mst.v20i3.3065
- [15] S. Lee, W. Shim, J. Kim, Y. Kim, and W. Kwon, "Effect of sintering-additive composition on fracture toughness of liquid-phase-sintered SiC ceramics," *J. Mater. Sci. Lett.*, no. 20, pp. 143–146, 2001. DOI: 10.1023/A:1006754708677
- [16] J. H. Lee, D. Y. Kim, and Y. W. Kim, "Grain boundary crystallization during furnace cooling of  $\alpha$ -SiC sintered with Y<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO," *J. Eur. Ceram. Soc.*, vol. 26, no. 7, pp. 1267–1272, 2006. DOI: 10.1016/j.jeuceram.2005.01.050
- [17] K. J. Kim, K. Y. Lim, and Y. W. Kim, "Influence of Y<sub>2</sub>O<sub>3</sub> addition on electrical properties of  $\beta$ -SiC ceramics sintered in nitrogen atmosphere," *J. Eur. Ceram. Soc.*, vol. 32, no. 16, pp. 4401–4406, 2012. DOI: 10.1016/j.jeuceram.2017.07.001
- [18] M. L. Xie, D. L. Luo, X. Bin Xian, B. Y. Leng, C. Chang'an, and W. Y. Lu, "Densification of nano-SiC by ultra-high pressure effects of time, temperature and pressure," *Fusion Eng. Des.*, vol. 85, no. 7–9, pp. 964–968, 2010. DOI: 10.1016/j.fusengdes.2009.09.003
- [19] P. Yonathan, J. H. Lee, D. H. Yoon, W. J. Kim, and J. Y. Park, "Improvement of SiCf/SiC density by slurry infiltration and tape stacking," *Mater. Res. Bull.*, vol. 44, no. 11, pp. 2116–2122, 2009. DOI: 10.1016/j.materresbull.2009.07.004